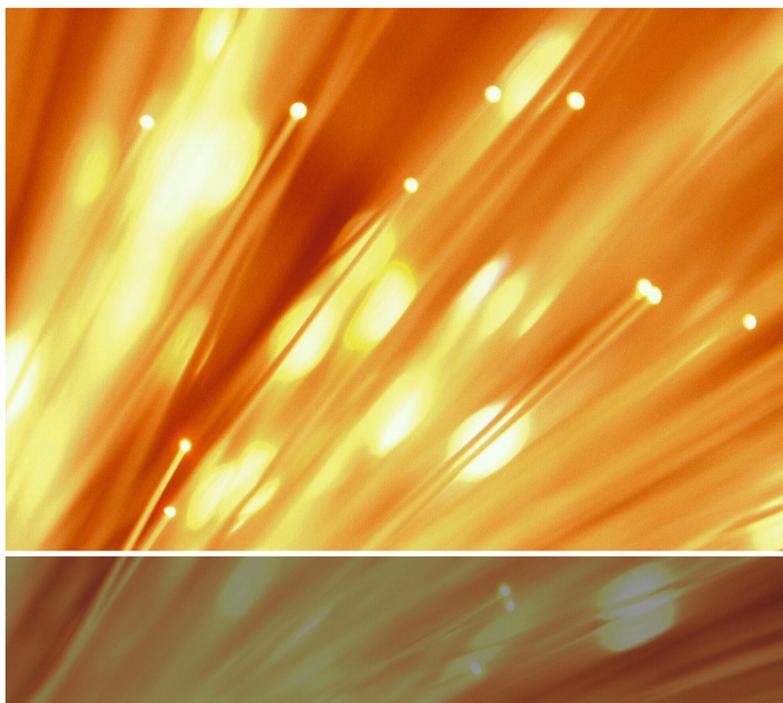


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# Electron Beam Curing of Composites



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# 1 Introduction to Electron Beam Curing of Composites

## 1.1 Principles of the Technique

Electron beam curing is based on the principle that fast electrons have the ability to initiate chemical changes in the material. The absorption of accelerated electrons in matter, with typical energies in the keV and MeV range, results on the initiation of secondary electrons as a consequence of the energy degradation process. These electrons enter into a Coulomb interaction with the atoms or molecules of the absorber, which finally leads to the formation of radicals, ions, trapped electrons, and an excited state of molecules or atoms [1].

Polymeric substances, which are predominantly high molecular weight organic compounds, such as plastics and elastomers (rubber), respond to radiation in several ways. Depending on the irradiation energy, these materials can either undergo degradation or chain cross-linking.

On the other hand, electron beam irradiation can also be employed to prepare polymers from monomers or from oligomers (essentially very low molecular weight polymers). In almost all of these reactions, a liquid (reactive resin) is converted into a solid more or less instantaneously. This transformation of monomers, oligomers, and polymers by irradiation to a rigid body is referred to as curing.

A wide range of high performance fiber reinforced polymers is currently based on thermosetting matrices, which are mainly a liquid reactive resin such as polyester, vinyl ester, epoxy, or bismaleimide resin. Thermosetting composites are cured at either ambient or elevated temperatures, and a hard solid is obtained due to the formation of a three-dimensional chemical cross-linked network. Typically, the use of radiation crosslinking decreases the curing time considerably, and allows processing at ambient temperature. Moreover, the use of high-energy electron beams allows the curing of thick fiber reinforced thermosetting composites. For instance, parts having a thickness up to 4 cm can be cured using a double-sided irradiation process.

Studies regarding electron beam curing of polymers have been conducted since the 1960s, mainly by Charlesby and Chapiro [2, 3], and in particular the field of electron beam curing of thermosetting composites has been investigated since the 1970s. Saunders and Singh [4] have been working on EB-curing of numerous resins, such as acrylated epoxies. They have not only studied the properties of the EB-cured composites, but have also investigated the effect of electron beam treatment on resins, fibers, and on the fiber sizing. Concerning the manufacture of such composites, Beziers et al. [5] have published a number of papers on filament wound electron beam cured composites.

There are a number of advantages of using electron beam irradiation to cure composites compared to conventional thermal processing. The reduced overall manufacturing costs,

discussed in Section 4.1, is one of the major driving forces for the development of this new technology.

Moreover, the opportunity to work at room temperature is one of the main advantages of this process and it derives from the fact that the reaction mechanism involved in the polymer curing does not require thermal activation. In particular the conservation of room temperature during the process allows the use of less expensive materials for the molds, and above all, it reduces the formation of internal stresses in the product, caused by the difference in the expansion of the cured system and the mold. Nevertheless, during irradiation the temperature of the materials can increase depending on different parameters. Heat evolution in the material is caused by the occurrence of two phenomena: the absorption of radiation energy and the exothermic polymerization reaction [6].

Curing times of composites are much shorter when using electron beam curing, leading to increased production rates. Furthermore, the resins (which are not designed to cure thermally) are more stable and thus have longer shelf life, making low temperature storage unnecessary. In addition, the electron beam process has environmental advantages because the materials have reduced emission of volatiles in comparison to typical thermally curable resins [7].

Finally, electron beam processing is a continuous operation, and components can be electron beam treated immediately after they have been produced. This continuous operation makes production scheduling and inventory control easier and reduces the number of identical molds needed to economically manufacture products, as compared to using a batch process, such as thermal curing in an autoclave.

## 1.2 Chemical Aspects of the Curing Reaction

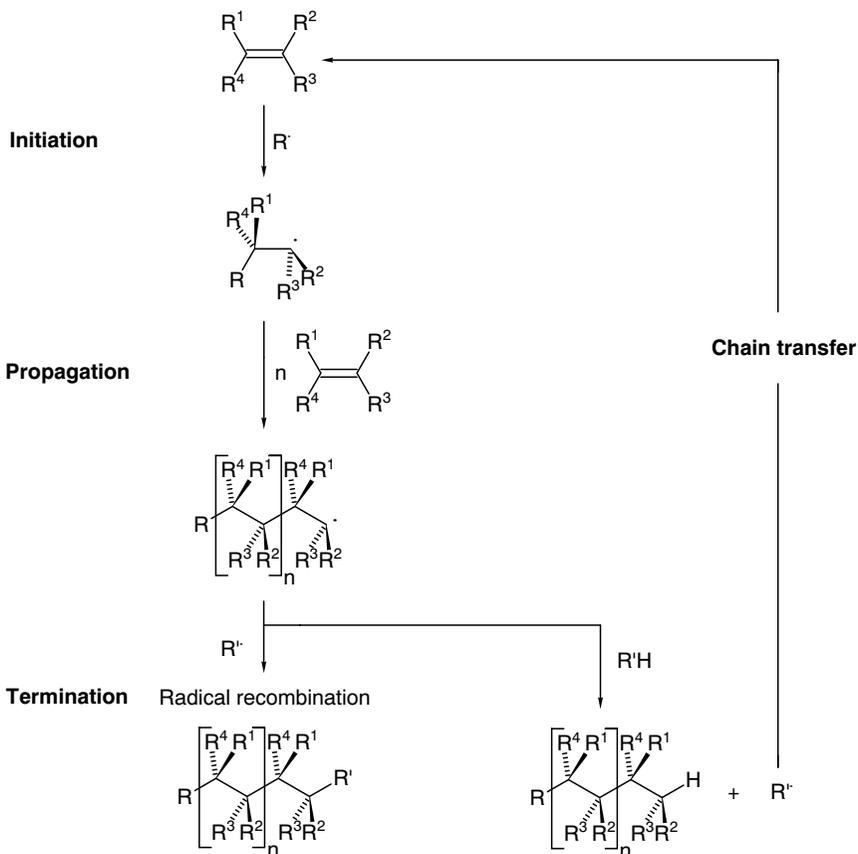
High-energy electrons, when impacting matter, generate ionic species, free radicals, and molecules in excited states capable of initiating and sustaining polymerization. Depending on the chemistry of the resin system being irradiated, polymerization can proceed via a free radical or a cationic mechanism [8].

There are, however, some marked differences between cationic and free radical polymerizations. For example, there is nearly a first-order dependency of the polymerization rate on the irradiation intensity in cationic polymerizations, rather than the half-order relationship that is observed in free radical polymerizations. The rates of cationic polymerizations are also highly temperature dependent, whereas the rates of free radical polymerizations display little temperature dependence. The most striking difference between these two polymerization mechanisms is the ability of cationic polymerizations, once initiated, to proceed further in the absence of radiation. Most free radical polymerizations cease within a millisecond after irradiation shutdown because of rapid termination [9]. In the next sections, these two polymerization mechanisms will be presented in detail.

### 1.2.1 Free Radical Polymerization

Radicals can have lifetimes ranging from a sub-second timescale up to long-term persistence, depending on their chemical environment. Free radicals are generally very reactive and therefore free radical polymerization [10, 11] reactions exhibit frequently low selectivities. Consequently, several side reactions can occur and thus radical reactions are usually not as well defined as ionic polymerization reactions.

The polymerization of monomers containing double bonds is often conducted thermally by free radical polymerization. The reaction cascade comprises three major steps: initiation, propagation, and termination (Fig. 1.1). Initiation is usually triggered by the use of peroxides. These peroxides homolytically decompose upon heating to form free radicals that add to the monomer, thus transferring the active site. Such initiators are not required for electron beam initiation since the irradiation of vinyl-containing monomers, such as acrylates and methacrylates, leads to the cleavage of double bonds to generate free radicals.



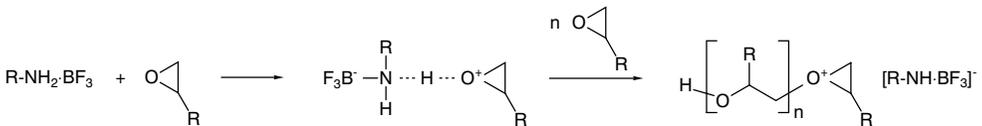
**Figure 1.1:** Dominating reactions in the free radical polymerization of unsaturated monomers

Polymerization proceeds via propagation steps that involve successive addition of vinyl-containing monomers to the active radical centre. Termination occurs, similarly to thermally curable systems, by several processes including radical recombination, chain transfer, disproportionation, and radical trapping. However, the polymerization induced by high dose rate electron beam curing can differ significantly from polymerizations initiated via thermal decomposition of initiators, as the high concentration of initiating radicals in electron beam curing affects the balance between propagation and termination [12].

A major concern of free radical polymerization and cross-linking processes regards the fact that this reaction can be inhibited by oxygen, which can react with the initiating radicals as well as the propagating free radical chains. The reaction with oxygen either prevents chain propagation or simply terminates the propagating chain. Accordingly, the residual oxygen concentration in the irradiation zone must be lowered to 100–1000 ppm (depending on the thermosetting system) by inert-gas purging [1].

### 1.2.2 Cationic Polymerization

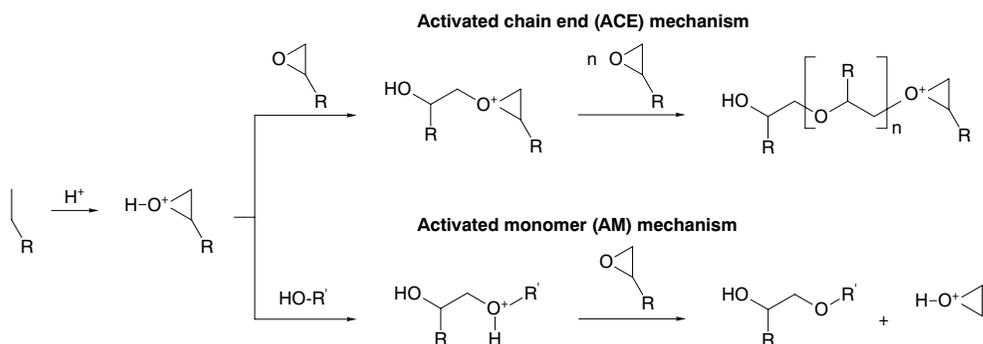
A series of monomers such as olefins, vinyl ethers, or heterocyclic compounds like cyclic esters and ethers can be polymerized via cationic mechanisms [13–15] using directly Brønsted or Lewis acids as initiators or species that generate such acids upon energy impact either by heating or irradiation. In this context, sophisticated studies on the thermal curing of epoxy resins by cationic polymerization have been carried out employing boron trifluoride-amine complexes as initiators and it has been shown that these Lewis acid-base adducts exhibit high efficiencies [16–24]. According to the mechanism outlined in Fig. 1.2, polymerization is initiated by protonation of the epoxide ring. The resulting oxonium species are able to attack further epoxy groups, thus starting propagation reactions.



**Figure 1.2:** Cationic polymerization of epoxides initiated by boron trifluoride-amine complexes

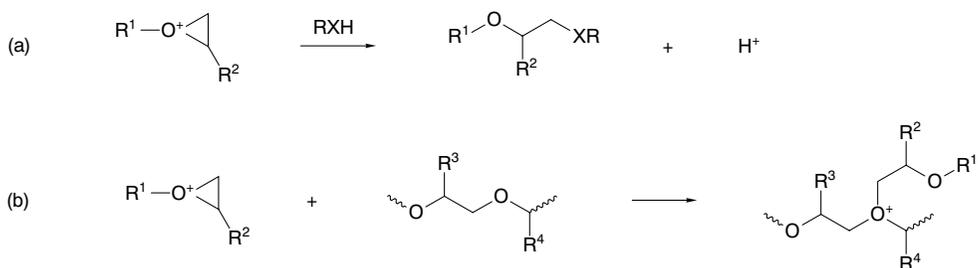
Polymerization propagation can proceed via two competing pathways (Fig. 1.3) referred to as the activated chain end (ACE) and the activated monomer (AM) mechanism. The former is characterized by monomer addition to the chain end, whereas the latter comprises alternately reactions of the protonated monomer with hydroxyl containing species or other proton donors and proton transfer reactions to the monomer. The activated center is switching continuously between the growing polymer chain and the monomer, thus maintaining a living polymerization. The mechanisms can proceed simultaneously and their extent mainly depends on the monomer/proton donor ratio as well as the polymerization stage.

Termination of cationic polymerization can occur by reaction of cationic species with nucleophiles and therefore the nature of further components in the compositions can play a major



**Figure 1.3:** Cationic polymerization of epoxides via ACE and AM pathways

role. The basicity and nucleophilicity of the involved species should be kept at a minimum and this applies particularly to anions present in the formulations. Non- or at least weakly basic anions such as  $\text{SnCl}_5^-$ ,  $\text{TiCl}_5^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$  or  $\text{SbF}_6^-$ , which are frequently employed as counterions in cationic initiators, are suitable and can shield cationic propagating species from nucleophiles, e.g., water, by ion-pair formation, thus reducing termination reactions. Chain transfer is another prominent termination process (Fig. 1.4) that is promoted by protic species such as water or alcohols. These can react with cationic centers, thus generating protons that can accomplish again monomer activation and polymerization initiation. Chain transfer can also occur by inter- and intramolecular reactions of active centers with oxygen atoms in the already grown polyether chain. In contrast to radical-mediated reactions, these cationic curing reactions do not suffer from inhibition by molecular oxygen.



**Figure 1.4:** Chain transfer reactions in the cationic polymerization of epoxides by reactions of propagating species either with protic species (a) or oxygen in the polymer chain (b)

It is assumed that radiation induced cationic polymerizations proceed via similar pathways. However, due to radical and ionization reactions by direct interaction of the monomers and/or initiators with high energy radiation, these processes can be, from a mechanistic point of view, much more complicated and, naturally, strongly depend on the radiation type. Since the discovery of highly efficient onium salt initiators for UV induced cationic polymerizations (see also Chapter 2), these light induced processes have been investigated in detail and the

technology became well-established with numerous applications, e.g., in the fields of photoresists, printing inks, stereolithography, or adhesives [25–28]. Some research groups studied also curing by  $\gamma$ -irradiation, employing monomers such as epoxides [29–35], vinyl ethers [36], styrenes [37–39], or THF [40] and it was shown by direct comparison that similar results can be obtained using electron beam irradiation [29, 33].

Employing the latter technology, remarkable progress was made during the last years [5, 41–45] and activities in this research field concentrate on the cationic polymerization of commercially important epoxy resins ranging from mechanistic studies on a molecular level [46–50] to applications such as the preparation of high-performance composites [41–45, 51–53]. A significant stimulus was certainly the finding that classical initiators, originally developed for UV curing, exhibit also high efficiencies in electron beam processing. An interesting post-irradiation phenomenon observed for the electron beam curing of cationically polymerizing systems is that curing takes place even after exposure to the electron beam. A plausible explanation for this phenomenon could be related to the ions generated during radiation. The cationic cure process by electron beam irradiation can therefore be divided into two parts, “dark” reactions (reactions that occur after irradiation) and “light” reactions (reactions that occur during irradiation) [54]. The “light” reactions are characterized by a very rapid response to irradiation, with a reaction rate that increases approximately linearly with the applied dose, at least within the limitation of dose rate and total dose per pass. These reactions are also characterized by a rapid rate decay after irradiation, with a decay time constant that appears to follow an Arrhenius relationship. “Dark” reactions show a behavior quite different from that of “light” reactions. “Dark” reactions do not decay on the same time scale as the “light” reactions, although they possibly also have a finite life time. It is also reasonable to assume that “dark” reactions proceed unabated during irradiation while “light” reactions superpose these “background” reactions.

### 1.2.3 Network Formation

For both afore-mentioned polymerization mechanisms, free radical and cationic, the use of electron beam processing leads to a crosslinking reaction and therefore results in the formation of a compact and rigid network.

The crosslinking reactions are controlled by reaction diffusion, instead of the dominance of molecular diffusion, and therefore the crosslinking reaction rate gradually decreases. The reaction rate rapidly slows down when the glass transition temperature ( $T_g$ ) of the cured resin reaches the curing temperature. This event is known as vitrification. In addition, the increasing gel fraction must reduce the number of curable functional groups in the network due to saturation effects of crosslinking. Therefore, at this stage, the unit radiation dose brings about less curing reaction [55].

Although electron beam curing is a non-thermal activated cure process, it is known that during irradiation the temperature of the material increases mainly due to the exothermic behavior of the polymerization reaction. The effect of polymerization reaction heat can therefore be favorably used to obtain high conversion, as it delays vitrification, where the mobility of molecules